OSMOTIC PRESSURE MEASUREMENTS OF LEVULOSE SOLUTIONS AT THIRTY DEGREES

DISSERTATION

Submitted to the Board of University Studies of The Johns Hopkins University in conformity with a requirement for the Degree of Doctor of Philosophy.

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By
JOHN MILTON BLOCHER, JR.,

Baltimore, 1916.

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I. ACKNOWLEDGMENT.

The author is glad to avail himself of this opportunity to express his appreciation to Prof. Morse, the late Prof. Jones, Dr. Lovelace, Dr. Reid, Dr. Frazer, Dr. Holland, and Dr. Schwartz for their valuable instruction.

The author is especially grateful to Prof. Morse, at whose suggestion and under whose guidance this investigation was undertaken and carried out.

The author is under obligation to Dr. Holland for much valuable advice and assistance.

The author is indebted to Dr. Frazer for much inspiration, and for his kindly interest in the work.

THE OSMOTIC PRESSURE MEASURMENTS OF LEVULOSE SOLUTIONS AT THIRTY DEGREES

II. LEVULOSE SOLUTIONS.

The levulose, which was used in this investigation was obtained in Germany. The preliminary purification in which the penta-acetate was made, giving the pure sugar upon hydrolysis, was performed by Dr. C. S. Hudson, of the Bureau of Chemistry at Washington, D. C. The author wishes to acknowledge his obligation to Dr. Hudson and his co-workers for this valuable material.

There remained in the sugar some traces of acetic acid. Our solute was freed from the traces of acetic acid by the following method, depending upon the fact that levulose is practically insoluble in cold absolute alcohol.

One hundred grams of the once recrystallized sugar were dissolved in fifty cubic centimeters of 75% alcohol which had been previously warmed on a steam bath. Seventy-five cubic centimeters of absolute alcohol were added to this solution. It was necessary, in some cases, to add a little animal charcoal and a few cubic centimeters of washed alumina to remove a slight turbidity. After filtering the mixture, twenty-five cubic centimeters of absolute alcohol were added to the clear filtrate. Upon "seeding" the solution, the sugar was precipitated. The crystallization was carried on in a dessicator with frequent stirring. The yield was about 50% of the original material used and the specific rotation was found to be 92°.0, the same value as the one assigned to pure levulose by the Bureau of Chemistry at Washington.

Solutions of levulose are peculiar in that they exhibit a change in specific rotation with change in temperature. A solution which is taken from a cell after having given

a measurement, is examined in a saccharimeter to determine whether or not it has undergone a change in concentration. It was found necessary, because of this change in rotation with change in temperature, to retain a sample of the original solution for the purpose of comparing its rotation, under the same conditions of temperature, with the rotation of the solution which was taken from the cell.

All solutions were made by dissolving a gram molecular weight of the sugar or a decimal part of the same in one thousand grams of water. This weight normal system of making up solutions is used in preference to the volume normal method for the following reasons:[1]

A volume normal solution, made by dissolving a gram molecular weight of the substance, or a decimal part of the same, in water and diluting to one litre is correct for merely analytical purposes. It is "both disadvantageous and illogical whenever any phenomenon is to be studied in which the influence of the solvent upon the solute is involved." "In cases of the latter kind, the true concentration of the solution is determined by the numerical ratio of the molecules of the solute to those of the solvent, rather than by the number of solute molecules in a given space."[2]

Difficulties are encountered when an attempt is made to make up a less concentrated solution by diluting a more concentrated one. For example, "Suppose a 0.1 volume normal solution of cane sugar to be made up by diluting 100 cubic centimeters of a normal solution to 1000 cubic centimeters. With respect to the relative numbers of solute molecules contained in equal volumes, the new solution is one-tenth as concentrated as that from which it was made, but with respect to the ratio of solute to solvent molecules, namely: 1:44.1 and 1:544.1, the concentration of the diluted solution is not 0.1 but 0.081 normal.[3]

1 For further discussion of the advantages of the weight normal system, reference is made to the Monograph by Prof. H. N. Morse, Carnegie Publication, No. 198, Chap. V.
2 Ibid., Chap. V., p. 100.
3 Ibid., p. 100.

The numerical ratio of solute to solvent molecules in a cane sugar volume normal solution at 30 degrees is about 1:44.1. At the same temperature, the numerical ratio of solute to solvent molecules in a volume normal solution of glucose is 1:49.2. Thus we see that the cane sugar solution is 11.5% more concentrated than the glucose solution, although equal volumes of the two solutions contain the same number of solute molecules. This difference would amount to 3.7 atmospheres when stated in terms of osmotic pressure.

The practice of employing the volume of the solvent as the standard for the computation of the gas pressure of the solute made it necessary to make a correction corresponding to the term "b" in the Van der Waals equation for gas pressure. The weight normal system gives us a means of correcting for the volume of the solute molecules. However, the true volume of the solvent in solution cannot be known accurately until the extent of the hydration of the solute is determined at all temperatures.

III. DESCRIPTION OF APPARATUS

A. THE CELLS.[4]

A cell, in which the true osmotic pressure of a solution may be measured, must meet the following conditions:

(1) It must have a uniformly strong wall.

(2) It must be absolutely free from air blisters.

(3) It must have an excessively fine and perfectly uniform texture of wall.

The high pressure, to which the cell is subjected in the process of measuring, make the first requirement absolutely imperative.

Air blisters, communicating with the interior of the cell wall, would cause a local deposition of the membrane in these regions. Experience has shown us that a membrane, in order to be very strong, must be deposited just within the mouths of the pores of the interior wall of the cell.

The pores of the wall must be so fine that the more mobile cation may pass nearly through them while the slower anion is just entering the mouths of the pores on the interior wall. In this way we secure an infinite number of plugs of the active membrane material supported by the whole body of the cell wall. These plugs are driven into the pores so tightly, by means of the electric current, that no amount of pressure will dislodge them. The electrolytic method of depositing membranes, devised by Prof. Morse, is far superior to the old method of Pfeffer.

A mixture of equal parts by weight of the finest portions of a fire clay, obtained from Dorsey, Md., and of a ball clay from Edgar, Fla., was found to give the best results in cell making. The clays were first elutriated and the finest portions were passed through No. 14 and No.

4 Ibid., Chap. I.

16 bolting cloth, containing 19,000 and 24,000 holes to the square inch respectively. After the particles were filtered and allowed to dry thoroughly, equal parts by weight were mingled by sifting, and then by mixing with distilled water in large cylinders. The mixture of the two clays and water was kept in constant agitation while the particles were again passed through the No. 14 and then through the No. 16 bolting cloth. The repeated bolting insured a very intimate mixture of the clays and particles of desired fineness were obtained.

Water was removed from the mixture of the clays until it had the consistency of ordinary putty and cylinders were formed under pressure[5] of twenty tons to the square inch. A cylinder, which is formed by any method employing a smaller pressure, produces a cell whose wall is too porous. These cylinders were placed upon a lathe and the cells of desired shape and size were turned out with tools of special form. The cells were then baked at the temperature of Seger cone No. 7 (1270°) and afterwards rebaked at the temperature of cone No. 8 (1290°). Before the upper end of the cell may be glazed it must be ground to required form on a lathe. A small, rapidly rotating carborundum wheel was used for this work.

Air must be entirely removed from the pores of the cell before the membrane may be deposited. This is accomplished by electrolyzing a 0.005N solution of lithium sulphate in such a way that the cation, which always carries a large "atmosphere" of water, is driven inwardly through the wall of the cell. After the air has been removed, the salt solution is replaced by pure distilled water which is renewed frequently. This final electrolysis serves to remove the lithium sulphate from the cell pores and it is continued until the conductivity equals that of distilled water. The cell is then placed in a saturated solution of thymol water and kept there until required for the process of depositing the membrane.

5 Ibid., Chap. I, p. 9.

B. DEPOSITION OF MEMBRANES.[6]

The membranes of copper ferro-cyanide are deposited in a constant temperature bath especially constructed for that purpose. A circular anode of copper is placed in a vessel containing a 0.01N solution of copper sulphate. The cell is placed within the circular anode and is closed by a rubber stopper carrying the cathode of platinum, an overflow tube and a funnel whose stem nearly reaches the bottom of the cell. A solution of 0.01N potassium ferro-cyanide is placed within the cell by means of the funnel and the membrane is deposited in the pores of the cell wall under a pressure of 110 volts. The solution of potassium ferro-cyanide is replaced at intervals of three minutes to prevent an accumulation of free alkali, which acts disasterously upon the membrane. The resistance of the membrane is noted from time to time by means of a milliammeter. During the course of deposition a gradual increase in the resistance will be noticed. The resistance will remain constant at its maximum for a short time and then it will decline. The electrolysis is interrupted just before the decline in resistance takes place. The cell is then emptied, washed internally and externally, and allowed to soak in thymol water for three days.

Thymol is toxic toward a strain of pencillium glaucum, a nitrogen consuming fungi, which readily infect the membrane. After the soaking period, the cell is again subjected to the membrane forming process. The subsequent "runnings" will cause the membrane to show an increase in resistance.

When the resistance is thought to be sufficiently great, the cell is "set up" with a concentrated cane sugar solution. This part of the cell's development is called, "seasoning under pressure," that is, the cell is filled with the cane sugar solution which contains a little dissolved potassium ferro-cyanide and is closed by a manometer. A solution of copper sulphate, which is osmotically equiva-

6 Ibid., Chap. IV.

lent to the amount of dissolved potassium ferro-cyanide, is placed on the outside of the cell. If there are any weak places in the membrane, the pressure will cause a rupture and the membrane formers will mend the broken places. Very often one period of "seasoning under pressure" is sufficient to produce a cell which will measure the true osmotic pressure of a solution and which will not allow the cell contents to become diluted. If this should not be the case, the cell is again subjected to the "running" and "soaking" process. During these operations, the cells and the solutions of membrane formers are maintained at the temperature at which the cells are subsequently used. The cells must never be exposed to any great or rapid changes in temperature.

C. RECOVERY OF OLD CELLS.

A cell will become intolerably slow in its action after a time due to the fact that its membrane is old and perhaps too thick, because of the repeated reinforcement. It is then desirable to remove the old membrane and replace it by a new and more active one. The slowness with which an old cell comes into equilibrium is the only undesirable feature for a cell which has once "measured" will continue to give good service while it is in existence provided it is not injured in other ways.

Pfeffer[7] recommends the following method for the removal of membranes. The cell is allowed to soak in a solution of potassium hydroxide to which a little Rochelle salt has been added, and afterwards in water; then in hydrochloric acid and again in water. This procedure will remove the membranes with ease but we have not been very successful in building a good membrane in a cell after subjecting it to this treatment.

A modification[8] of this method was tried in this laboratory in which the potassium hydroxide and the hydrochloric acid were omitted. The soluble salts which remained in the cell wall after soaking in water were re-

7 "Osmotische Untersuchungen," 12.
8 Ibid., Chap. V, p. 93.

moved by electrolysis. This method required a long period of time, and, on the whole, was not very successful. The method of grinding off the interior surface of the cell wall, by means of a rapidly revolving carborundum wheel, gave only fair results.

A very successful method was developed recently in this laboratory. A one-fifth normal solution of potassium acid tartrate is prepared and made alkaline by potassium hydroxide. The old cells are soaked in this solution, which is frequently renewed, until the blue coloration is no longer noticeable. The cells are then washed and placed in a 5% solution of nitric acid until the slight blue coloration again disappears. After the cells are washed they are subjected to electrolysis in distilled water until copper no longer deposits upon the cathode. They are then reburned at the temperature of cone No. 7, the air is removed by the lithium sulphate method, and the new membrane is deposited in the usual manner.

Of the seventeen cells treated in this manner we secured thirteen which are now giving measurements and four which are giving promising results. These cells are termed the "R" series and a number have been used successfully in the measurement of the osmotic pressures of levulose solution at thirty degrees.

D. MANOMETERS.[9]

The manometers, which were used for measuring the pressures in the following experiments were made of thick walled glass tubes having an external diameter of about six millimeters. The diameter of the bore ranged from 0.45 to 0.72 millimeters and the length of the calibrated portion was from 400 to 500 millimeters.

There are three reasons for using tubes of small bore.[10] (1) After filling the manometer with nitrogen it is necessary to enclose a small thread of mercury within the uppermost portion of the tube because, in "sealing off" a manometer, the caliber of the tube in the region of the

9 Ibid., Chap. II.
10 Ibid., p. 27.

seal is affected to an unknown extent. Should the bore have a large diameter, this small thread of mercury would become dislodged when the tube is subjected to tapping during the determination of the volume of the enclosed gas. (2) The volume of the included gas is so small that its compression does not produce a great dilution of the solution within the cell. (3) Small bore manometers require relatively small volumes of mercury.

Small bore manometers have these disadvantages.[11] (1) There is more difficulty in dealing with a meniscus in a tube of small bore. (2) A tube of small bore has a large capillary depression which varies greatly with slight irregularities of bore. (3) The movement of the mercury in such a tube is more liable to be influenced by small irregularities or by impurities which may be fused into the interior wall of the tube.

Two fine lines are etched upon the tube before the calibration is begun. These lines extend completely around the instrument and they are so fine that they may just be seen by the naked eye. All subsequent readings are referred to these "scratches"[12] for the tube is devoid of further graduation. The "lower scratch" is placed near the lower end of the calibrated portion of the tube and the "upper scratch" is placed near the upper end and above the widened section of the bore. The tube is placed in a horizontal position upon a dividing engine, whose screw has been carefully compared with the graduated meter scales which are employed in the measuring of osmotic pressures.

"The calibration is commenced at the lower scratch and consists in setting the (short) thread of mercury exactly end to end, and determining its length, until the thread has passed the upper scratch. It is run out of the tube and weighed. Then the whole of the calibrated portion of the tube is filled with mercury, the thread measured and again run out and weighed. From the length and weight of the long thread, the mean diameter of the bore may be estimated; and from the observations on the

11 Ibid., Chap. II, p. 27.
12 Ibid., p. 29.

length of the short thread in the different parts of the tube, a mean calibration unit is derived, and a curve of corrections constructed. Finally, a mean value for the double meniscus is obtained from the length and weight relations of the long and short threads. If we multiply the weight of the short thread by the number of times its length is contained in that of the long thread, the difference is the weight of the mercury which would be required to fill the meniscus spaces which were left vacant in setting the short thread end to end along the tube. Converting this difference in weight into volume and dividing by the number of settings less one, we obtain a mean correction for a double meniscus, which is the meniscus correction to be applied in all measurements of pressure."[13]

The above method is used for manometers without the widened portion in the bore. The method for large volume manometers differs in only one respect, the capacity of the widened portion must be accurately determined as a whole and afterwards in terms of the calibration unit. The correctness of all previous work may be tested[14] in two ways so that its accuracy can not be doubted.

A series of thick walled glass bulbs, three in number, are sealed on to the calibrated tube. "The bulb nearest the calibrated end serves as a reservoir in which the nitrogen, when under diminished pressure, may expand without danger of escaping from the instrument." "The bulbs nearest the cell serve as reservoirs for the mercury which is to be driven forward in compressing the nitrogen, and their total capacity is therefore, to be regulated by the volume of the gas under ordinary conditions and the maximum pressure to be measured."[15] The bulb next to the cell is provided with a trap which prevents the mingling of the sugar solution with the mercury in the uncalibrated portions of the manometer.

The instrument is filled with mercury to a desired level and is connected to a side tube, containing mercury, by

13 Ibid., Chap. II, pp. 31-33.
14 Ibid., Chap. II, p. 33.
15 Ibid., p. 37.

means of a flexible rubber tube. This system is placed in a constant temperature bath and the capillary depression is determined at different points in the bore. A curve is plotted, and, assuming that the change in capillary depression between the points is regular, the values for many points are secured. This procedure is of great importance since the values obtained are used "in determining the volume of the enclosed nitrogen under standard conditions of temperature and pressure" and also "in correcting its volume under an unknown pressure, which, i. e., osmotic pressure is a quotient of the two volumes."

Unusual care is taken in the purification[16] of the mercury which is used in the manometers and thermostats. (1) The commercial product is allowed to run through a few pin holes in a filter paper. This removes the coarse dirt. (2) It is heated to its boiling point in a retort, to which has been fused a long glass tube, while air is forced through the metal. After four hours the metal is freed from the scum of its oxides by filtration. (3) It is distilled in a partial vacuum. (4) The distillate is washed by the method of Lother Meyer, modified by Hildebrand, in which the very fine droplets of mercury are carried by gravity through distilled water containing 2% nitric acid and 2% mercurous nitrate. The washing is repeated many times. (5) After it has been washed with distilled water and thoroughly dried it is again distilled under diminished pressure but not in the still used for the first distillation.

The gas employed in the manometers is pure nitrogen. It is obtained by passing air through an alkaline solution of para-gallol and then, in the order named over heated copper oxide, heated copper, calcium chloride, potassium hydroxide and resublimed phosphorus pent-oxide. A detailed and interesting account of the process of filling manometers may be found on pace 46 in the Monograph by Prof. Morse. The volume of gas in the manometer is then determined under approximate atmospheric pressure and

16 Ibid., Chap. II, p. 28.

then reduced to standard conditions of temperature and pressure. The instrument may now be used for the measurement of osmotic pressures after being attached[17] firmly to a cell containing the sugar solution of desired concentration.

E. REGULATION OF TEMPERATURE.[18]

It is of utmost importance that the whole system, i. e., solution, solvent, cell and manometer be kept at constant temperature during the process of measuring osmotic pressure. A cell, filled with a solution of known concentration and closed by a manometer is not unlike a thermometer. Any slight fluctuation in temperature is always followed by "thermometer effects"[19] which are very detrimental to the success of an experiment because of three facts: (1) "The capacity of the closed osmotic cell is nearly a fixed quantity." (2) "Every change in the volume of the enclosed solution due to rise or fall in temperature is followed by a discharge or intake of solvent through the membrane, both of which acts also modify the volume and the osmotic pressure of the solutions." (3) "The passage of the solvent through the membrane, in either direction, is usually a much slower process than the changes in the volume of the cell contents which result from fluctuations in temperature."

The constant temperature baths used in this investigation were made to conform with the following principle:[20] "If all the water or air in a bath is made to pass rapidly (1) over a continuously cooled surface which is capable of reducing the temperature slightly below that which it is desired to maintain, then (2) over a heated surface which is more efficient than the cooling one but which is under the control of a thermostat; and (3) again over the cooled surface, etc., it should be practicable to maintain

17 Ibid., Chap. II, pp. 17-26.
18 Ibid., Chap. III.
19 For a discussion of the intricate phenomena concerned with "thermometer effects," reference is made to the Monograph, pp. 51-55.
20 Monograph, p. 56.

in the bath any temperature for which the thermostat is set, and the constancy of the temperature should depend only upon the sensitiveness of the thermostat and the rate of flow of the water or air."

The principle is the same whether the heating or the cooling surface is under the control of the thermostat. In the work at zero degrees, melting ice served both as a cooling surface and as a thermostat.

The thermostats used at thirty degrees were sufficiently sensitive, when used in the baths made to conform with the above principle, to maintain a constant temperature to within one-one-hundredth of a degree. This principle is the last word in temperature regulation, for there is a bath in this laboratory which will maintain a constant temperature to within one-one-thousandths of a degree. An especially sensitive thermostat is used.

The measurements of the osmotic pressures of levulose solutions at thirty degrees were taken in the baths especially well suited for work at the higher temperatures. They are made of heavy sheet brass. Each bath has an outer shell and an inner compartment. Between these two, water is kept in constant circulation in such a manner and direction that it will first flow over a cooler surface and then over a warmer surface of the bath. The heating surface was provided for by a number of 60 watt electric lamps in an equal number of compartments inserted within the water space. Each lamp, which serves as a "stove," is under the control of a relay; the series of relays is controlled by a master relay, which in turn is controlled by the thermostat which is placed in the circulating water and near the top of the bath. Sparking in the thermostat and relays is prevented by introducing a shunt of high resistance at the proper places.

The entrance to the inner bath is closed by (1) a plate glass door and (2) a hollow, metal door in two sections, the lower half of which is only opened when it is necessary to introduce or remove cells. A space of 40 millimeters, between the doors, is occupied by (1) a metal shield carrying on its upper half, a dozen smaller metal

strips or doors, anyone of which may be opened independently of the others for the purpose of reading the manometer.

The heat derived from the 60 watt lamps was sufficient to keep the baths at thirty degrees. In the work at higher temperatures, the gas burners beneath the bath are put into use. However, the elevated temperature, secured by means of these burners are kept a little lower than the temperature at which the bath is maintained. The difference or "temperature margin" is cared for by the lamps under the control of the thermostat.

IV. MEASUREMENTS.

TABLE I.

0.1 Wt. normal solution. Expt. 1 at 30°; Cell D_9. Resistance, 35,400 ohms. Manometer 27. Calc. gas pressure, 2.472 atms. Time of setting up cell Feb. 1, 1916. Barometer during final record: max., 1.011; min., 0.984. Total daily pressures:

Final Record.

Atms	Atms
Feb. 11, 3.554	Feb. 15, 3.537
Feb. 12, 3.540	Feb. 16, 3.537
Feb. 13, 3.517	Feb. 17, 3.534
Feb. 14, 3.517	Feb. 18, 3.519
	(8 days)

Mean total pressure Feb. 11, Feb. 18.....3.532 atms
Mean barom. pressure Feb. 11, Feb. 18.....1.002 atms
Mean osmotic pressure Feb. 11, Feb. 18 .....2.529 atms

TABLE II.

0.1 Wt. normal solution. Expt. 2 at 30°. Cell L_9. Resistance 24,400 ohms. Manometer 27. Calc. gas pressure, 2.472 atms. Time of setting up cell, Feb. 18, 1916. Barometer during final record: max., 1.004; min., 0.972. Total daily pressures:

Final Record.

Atms	Atms
Feb. 24, 3.523	Mar. 2, 3.489
Feb. 25, 3.505	Mar. 3, 3.480
Feb. 26, 3.494	Mar. 4, 3.476
Feb. 27, 3.483	Mar. 5, 3.473
Feb. 28, 3.486	Mar. 6, 3.481
Feb. 29, 3.492	Mar. 7, 3.487
Mar. 1, 3.497	(13 days)

Mean total pressure Feb. 24-Mar. 7 .....3.489 atms
Mean barom. pressure Feb. 24-Mar. 7 .....0.991 atms
Mean osmotic pressure Feb. 24-Mar. 7 .....2.499 atms

TABLE III.

0.2 Wt. normal solution. Expt. 1 at 30°. Cell I_9. Resistance 23,400 ohms. Manometer 24. Calc. gas pressure, 4.943 atms. Time of setting up cell, Feb. 10. 1916. Barometer during final record: max., 1.012; min., 0.990. Total daily pressures:

Final Record.

	Atms		Atms
Feb. 16,	6.081	Feb. 19,	6.051
Feb. 17,	6.072	Feb. 20,	6.051
Feb. 18,	6.058	Feb. 21,	6.051
			(6 days)

Mean total pressure Feb. 16-Feb.21 .....6.060 atms
Mean barom. pressure Feb. 16-Feb. 21 .....0.995 atms
Mean osmotic pressure Feb. 16-Feb. 21 .....5.065 atms

TABLE IV.

0.2 Wt. normal solution. Expt. 2 at 30°. Cell K_9. Resistance 25,000 ohms. Manometer 6. Calc. gas pressure 4.943 atms. Time of setting up cell, Feb. 10, 1916. Barometer during final record: max., 1.016; min., 0.984. Total daily pressures:

Final Record.

	Atms		Atms
Feb. 14,	6.044	Feb. 18,	6.023
Feb. 15,	6.043	Feb. 19,	6.019
Feb. 16,	6.040	Feb. 20,	6.002
Feb. 17,	6.035	Feb. 21,	6.017
			(8 days)

Mean total pressure Feb. 14-Feb. 21 .....6.028 atms
Mean barom. pressure Feb. 14-Feb. 21 .....1.000 atms
Mean osmotic pressure Feb. 14-Feb. 21 .....5.027 atms

TABLE V.

0.2 Wt. normal solution. Expt. 3 at 30°. Cell R_{15}. Resistance 78,500 ohms. Manometer 24. Calc. gas pressure 4.943 atms. Time of setting up cell, Jan. 28, 1916. Barometer during final record: max., 1.018; min., 0.994. Total daily pressures:

Final Record.

	Atms		Atms
Feb. 3,	6.008	Feb. 7,	6.029
Feb. 4,	6.022	Feb. 8,	6.022
Feb. 5,	6.015	Feb. 9,	6.030
Feb. 6,	6.009	Feb. 10,	6.028
			(8 days)

Mean total pressure Feb. 3-Feb.10 .....6.021 atms
Mean barom. pressure Feb. 3-Feb.10 .....1.006 atms
Mean osmotic pressure Feb. 3-Feb. 10 .....5.014 atms

TABLE VI.

0.3 Wt. normal solution. Expt. 1 at 30°. Cell N_9. Resistance 30,600 ohms. Manometer 24. Calc. gas pressure 7.415 atms. Time of setting up cell Jan. 13, 1916. Barometer during final record: max., 1.015; min., 0.994. Total daily pressures:

Final Record.

	Atms		Atms
Jan. 15,	8.631	Jan. 19,	8.580
Jan. 16,	8.532	Jan. 20,	8.594
Jan. 17,	8.538	Jan. 21,	8.598
Jan. 18,	8.560		(7 days)

Mean total pressure Jan. 15-Jan21 .....8.576 atms
Mean barom. pressure Jan. 15-Jan. 21.....1.007 atms
Mean osmotic pressure Jan. 15-Jan.21 .....7.569 atms

TABLE VII.

0.3 Wt. normal solution. Expt. 2 at 30°. Cell V_9. Resistance 47,000 ohms. Manometer 6. Calc. gas pressure 7.415 atms. Time of setting up cell, Jan. 13, 1916. Barometer during final record: max., 1.015; min., 0.997. Total daily pressures:

Final Record.

	Atms		Atms
Jan. 18,	8.509	Jan. 21,	8.598
Jan. 19,	8.564	Jan. 22,	8.594
Jan. 20,	8.590	Jan. 23,	8.512
			(6 days)

Mean total pressure Jan. 18-Jan. 23 .....8.561 atms
Mean barom. pressure Jan. 18-Jan. 23 .....1.008 atms
Mean osmotic pressure Jan. 18-Jan. 23 .....7.552 atms

TABLE VIII.

0.4 Wt. normal solution. Expt. 1 at 30°. Cell S_9. Resistance 29,000 ohms. Manometer 29. Calc. gas pressure 9.886 atms. Time of setting up cell, Jan. 13, 1916. Barometer during final record: max., 1.017; min., 0.997. Total daily pressures:

Final Record.

	Atms		Atms
Jan. 18,	11.014	Jan. 21,	11.020
Jan. 19,	11.034	Jan. 22,	11.024
Jan. 20,	11.030	Jan. 23,	11.031
			(6 days)

Mean total pressure Jan. 18-Jan. 23 .....11.025 atms
Mean. barom. pressure Jan. 18-Jan. 23 .... 1.009 atms
Mean osmotic pressure Jan. 18-Jan. 23 .....10.016 atms

TABLE IX.

0.4 Wt. normal solution. Expt. 2 at 30°. Cell R_1. Resistance 91,600 ohms. Manometer (1). Calc. gas pressure 9.886 atms. Time of setting up cell, Jan. 20, 1916. Barometer during final record: max., 1.016; min., 0.999. Total daily pressures:

Final Record.

	Atms		Atms
Jan. 27,	11.022	Jan. 31,	11.020
Jan. 28,	11.026	Feb. 1,	11.024
Jan. 29,	11.003	Feb. 2,	11.028
Jan. 30,	10.999		

(7 days)

Mean total pressure Jan. 27-Feb. 2 .....11.017 atms
Mean barom. pressure Jan. 27-Feb. 2 ..... 1.006 atms
Mean osmotic pressure Jan. 27-Feb. 2 .....10.011 atms

TABLE X.

0.5 Wt. normal solution. Expt. 1 at 30°. Cell M_9. Resistance 47,800 ohms. Manometer 27. Calc. gas pressure 12.358 atms. Time of setting up cell, Jan. 8, 1916. Barometer during final record: max., 1.017; min., 0.997. Total daily pressures:

Final Record.

	Atms		Atms
Jan. 9,	13.736	Jan. 12,	13.677
Jan. 10,	13.676	Jan. 13,	13.681
Jan. 11,	13.676		

(5 days)

Mean total pressure Jan. 9-Jan. 13 .....13.689 atms
Mean barom. pressure Jan. 9-Jan. 13 ..... 1.004 atms
Mean osmotic pressure Jan. 9-Jan. 13 .....12.685 atms

TABLE XI.

0.5 Wt. normal solution. Expt. 2 at 30°. Cell L_9. Resistance 31,200 ohms. Manometer 24. Calc gas pressure 12.358 atms. Time of setting up cell, Jan. 8, 1916. Barometer during final record: max., 1.017; min., 0.997. Total daily pressures:

Final Record.

Atms	Atms
Jan. 9, 13.695	Jan. 12, 13.628
Jan. 10, 13.655	Jan. 13, 13.617
Jan. 11, 13.628	

(5 days)

Mean total pressure Jan. 9-Jan. 13 .....13.644 atms
Mean barom. pressure Jan. 9-Jan. 13 ..... 1.004 atms
Mean osmotic pressure Jan. 9-Jan. 13 .....12.640 atms

TABLE XII.

0.5 Wt. normal solution. Expt. 3 at 30°. Cell Q_9. Resistance 55,000 ohms. Manometer 15. Calc gas pressure 12.358 atms. Time of setting up cell, Jan. 13, 1916. Barometer during final period: max., 1.015; min., 0.994. Total daily pressures:

Final Record.

Atms	Atms
Jan. 15, 13.748	Jan. 18, 13.599
Jan. 16, 13.561	Jan. 19, 13.619
Jan. 17, 13.592	Jan. 20, 13.644

(6 days)

Mean total pressure Jan. 15-Jan. 20 .....13.628 atms
Mean barom. pressure Jan. 15-Jan. 20 ..... 1.007 atms
Mean osmotic pressure Jan. 15-Jan. 20 .....12.621 atms

TABLE XIII.

0.5 Wt. normal solution. Expt. 4 at 30°. Cell X_9. Resistance 55,000 ohms. Manometer 56. Calc. gas pressure 12.358 atms. Time of setting up cell, Jan. 13, 1916. Barometer during final record: max., 1.015; min., 0.994. Total daily pressures:

Final Record.

Atms	Atms
Jan. 16, 13.549	Jan. 19, 13.530
Jan. 17, 13.509	Jan. 20, 13.475
Jan. 18, 13.524	

(5 days)

Mean total pressure Jan. 16-Jan. 20 .....13.517 atms
Mean barom. pressure Jan. 16-Jan. 20 ..... 1.005 atms
Mean osmotic pressure Jan. 16-Jan. 20 .....12.512 atms

TABLE XIV.

0.6 Wt. normal solution. Expt. 1 at 30°. Cell A_9. Resistance 33,300 ohms. Manometer 29. Calc. gas pressure 14.830 atms. Time of setting up cell, Jan. 6, 1916. Barometer during final record: max., 1.018; min., 0.997. Total daily pressures:

Final Record.

Atms	Atms
Jan. 8, 16.143	Jan. 11, 16.111
Jan. 9, 16.068	Jan. 12, 16.113
Jan. 10, 16.095	Jan. 13, 16.109

(6 days)

Mean total pressure Jan. 8-Jan. 13 .....16.104 atms
Mean barom. pressure Jan. 8-Jan. 13..... 1.006 atms
Mean osmotic pressure Jan. 8-Jan. 13 .....15.098 atms

TABLE XV.

0.6 Wt. normal solution. Expt. 2 at 30°. Cell D_9. Resistance 34,300 ohms. Manometer (1). Calc. gas pressure 14.830 atms. Time of setting up cell, Dec. 22, 1915. Barometer during final record: max., 1.015; min., 0.987. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 25,	15.985	Dec. 31,	16.082
Dec. 26,	16.053	Jan. 1, '16	16.061
Dec. 27,	16.078	Jan. 2,	16.104
Dec. 28,	16.104	Jan. 3,	16.100
Dec. 29,	15.998	Jan. 4,	16.108
Dec. 30,	16.056		

(11 days)

Mean total pressure Dec. 25, '15-Jan. 4, '16..16.066 atms
Mean barom. pressure Dec. 25, '15-Jan. 4, '16 0.998 atms
Mean osmotic pres. Dec. 24, '15-Jan. 4, '16 15.066 atms

TABLE XVI.

0.6 Wt. normal solution. Expt. 3 at 30°. Cell S_9. Resistance 55,000 ohms. Manometer 27. Calc. gas pressure 14.830 atms. Time of setting up cell, April 24, 1916. Barometer during final record: max., 0.996; min., 0.992. Total daily pressures:

Final Record.

	Atms		Atms
May 1,	16.065	May 5,	16.048
May 2,	16.048	May 5,	16.048
May 3,	16.048		

(5 days)

Mean total pressure May 1-May 5.....16.050 atms
Mean barom. pressure May 1-May 5 ..... 0.994 atms
Mean osmotic pressure May 1-May 5.....15.056 atms

TABLE XVII.

0.7 Wt. normal solution. Expt. 1 at 30°. Cell R_5. Resistance 53,000 ohms. Manometer 6. Calc. gas pressure 17.301 atms. Time of setting up cell, Dec. 20, 1915. Barometer during final record: max., 1.015; min., 0.987. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 24,	18.862	Dec. 30,	18.939
Dec. 25,	18.869	Dec. 31,	18.909
Dec. 26,	18.883	Jan. 1, '16	18.828
Dec. 27,	18.874	Jan. 2,	18.909
Dec. 28,	19.013	Jan. 3,	18.878
Dec. 29,	18.883	Jan. 4,	18.859
			(12 days)

Mean total pressure Dec. 24, '15-Jan. 4, 16 ..18.817 atms
Mean barom. pressure Dec. 24, '15-Jan. 4, '16 0.998 atms
Mean osmotic pres. Dec. 24, '15-Jan. 4, '16 17.819 atms

TABLE XVIII.

0.7 Wt. normal solution. Expt. 2 at 30°. Cell B_9. Resistance 44,000 ohms. Manometer 6. Calc. gas pressure 17.301 atms. Time of setting up cell, Jan. 6, 1916. Barometer during final record: max., 1.018; min., 0.997. Total daily pressures:

Final Record.

	Atms		Atms
Jan. 7,	18.520	Jan. 11,	18.766
Jan. 8,	18.600	Jan. 12,	18.761
Jan. 9,	18.612	Jan. 13,	18.766
Jan. 10,	18.781		
			(7 days)

Mean total pressure, Jan. 7-Jan. 13 .....18.686 atms
Mean barom. pressure Jan. 7-Jan. 13 ..... 1.006 atms
Mean osmotic pressure, Jan. 7-Jan. 13 .....17.679 atms

TABLE XIX.

0.7 Wt. normal solution. Expt. 3 at 30°. Cell R_{20}. Resistance 61,100 ohms. Manometer 53. Calc. gas pressure 17.301 atms. Time of setting up cell, Dec. 20, 1915. Barometer during final record: max., 1.015; min., 0.987. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 22,	18.607	Dec. 29,	18.655
Dec. 23,	18.615	Dec. 30,	18.453
Dec. 24,	18.608	Dec. 31,	18.555
Dec. 25,	18.602	Jan. 1, '16	18.513
Dec. 26,	18.604	Jan. 2,	18.500
Dec. 27,	18.608	Jan. 3,	18.544
Dec. 28,	18.578	Jan. 4,	18.547
			(14 days)

Mean total pressure Dec. 22, '15-Jan.4, '16 ..18.521 atms
Mean barom. pressure Dec. 22, '15-Jan. 4, '16 0.999 atms
Mean osmotic pres. Dec. 22, '15-Jan. 4, '16 17.562 atms

TABLE XX.

0.8 Wt. normal solution. Expt. 1 at 30°. Cell R_{14}. Resistance 137,500 ohms. Manometer 24. Calc. gas pressure 19.773 atms. Time of setting up cell, Dec. 17, 1915. Barometer during final record: max., 1.015; min., 0.987. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 20,	21.424	Dec. 27,	21.344
Dec. 21,	21.381	Dec. 28,	21.362
Dec. 22,	21.265	Dec. 29,	21.234
Dec. 23,	21.265	Dec. 30,	21.221
Dec. 24,	21.226	Dec. 31,	21.439
Dec. 25,	21.353	Jan. 1, '16	21.205
Dec. 26,	21.300	Jan. 2,	21.186
			(14 days)

Mean total pressure Dec. 20, '15-Jan. 2, '16 ..21.285 atms
Mean barom. pressure Dec. 20, '15-Jan. 2, '16 0.998 atms
Mean osmotic pres. Dec. 20, '15-Jan. 2, '16 20.301 atms

TABLE XXI.

0.8 Wt. normal solution. Expt. 2 at 30°. Cell R_2. Resistance 91,600 ohms. Manometer 27. Calc. gas pressure 19.773 atms. Time of setting up cell, Dec. 17, 1915. Barometer during final record: max., 1.015; min., 0.978. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 20,	21.172	Dec. 27,	21.261
Dec. 21,	21,172	Dec. 28,	21.164
Dec. 22,	21.202	Dec. 29,	21.098
Dec. 23,	21.208	Dec. 30,	21.196
Dec. 24,	21.237	Dec. 31,	21.125
Dec. 25,	21.237	Jan. 1, '16	21.050
Dec. 26,	21.237	Jan. 2,	21.073
			(14 days)

Mean total pressure Dec. 20, '15-Jan. 2, '16 21.174 atms
Mean barom. pressure Dec. 20, '15-Jan. 2, '16 0.999 atms
Mean osmotic pres. Dec. 20, '15-Jan. 2, '16 20.176 atms

TABLE XXII.

0.8 Wt. normal solution. Expt. 3 at 30°. Cell B_9. Resistance 50,000 ohms. Manometer 5. Calc. gas pressure 19.773 atms. Time of setting up cell Dec. 14, 1915. Barometer during final record: max., 1.007; min., 0.975. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 15,	20.959	Dec. 19,	21.044
Dec. 16,	21.025	Dec. 20,	21.187
Dec. 17,	21.072	Dec. 21,	21.199
Dec. 18,	21.149	Dec. 22,	21.255
			(8 days)

Mean total pressure Dec. 15-Dec. 22 .....21.111 atms
Mean barom. pressure Dec. 15-Dec. 22 ..... 0.999 atms
Mean osmotic pressure Dec. 15-Dec. 22.....20.111 atms

TABLE XXIII.

0.8 Wt. normal solution. Expt. 4 at 30°. Cell R_7. Resistance 157,000 ohms. Manometer 29. Calc. gas pressure 19.773 atms. Time of setting up cell, Dec. 17, 1915. Barometer during final record: max., 1.007; min., 0.995. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 20,	21.222	Dec. 25,	21.054
Dec. 21,	20.998	Dec. 26,	20.927
Dec. 22,	21.042	Dec. 27,	20.994
Dec. 23,	21.050	Dec. 28,	21.034
Dec. 24,	21.057		

(9 days)

Mean total pressure Dec. 20-Dec. 28 .....21.042 atms
Mean barom. pressure Dec. 20-Dec. 28 ..... 1.000 atms
Mean osmotic pressure Dec. 20-Dec. 28.....20.042 atms

TABLE XXIV.

0.8 Wt. normal solution. Expt. 5 at 30°. Cell R_{18}. Resistance 84,000 ohms. Manometer 39. Calc. gas pressure 19.773 atms. Time of setting up cell, Dec. 14, 1915. Barometer during final record: max., 1.007; min., 0.975. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 16,	21.546	Dec. 20,	20.940
Dec. 17,	21.086	Dec. 21,	20.926
Dec. 18,	20.908	Dec. 22,	20.959
Dec. 19,	20.808		

(7 days)

Mean total pressure Dec. 16-Dec. 22 .....21.024 atms
Mean barom. pressure Dec. 16-Dec. 22 ..... 0.999 atms
Mean osmotic pressure Dec. 16-Dec. 22.....20.025 atms

TABLE XXV.

0.9 Wt. normal solution. Expt. 1 at 30°. Cell B_9. Resistance 61,100 ohms. Manometer 6. Calc. gas pressure 22.244 atms. Time of setting up cell, Dec. 2, 1915. Barometer during final record: max., 1.007; min., 0.983. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 4,	23.800	Dec. 7,	23.854
Dec. 5,	23.887	Dec. 8,	23.810
Dec. 6,	23.899	Dec. 9,	23.799
			(6 days)

Mean total pressure Dec. 4-Dec. 9 .....23.841 atms
Mean barom. pressure Dec. 4-Dec. 9 ..... 0.998 atms
Mean osmotic pressure Dec. 4-Dec. 9 .....22.842 atms

TABLE XXVI.

0.9 Wt. normal solution. Expt. 2 at 30°. Cell G_9. Resistance 91,600 ohms. Manometer 27. Calc. gas pressure 22.244 atms. Time of setting up cell, Dec. 7, 1915. Barometer during final record: max., 1.004; min., 0.983. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 8,	23.772	Dec. 13,	23.825
Dec. 9,	23.846	Dec. 14,	23.863
Dec. 10,	23.825	Dec. 15,	23.863
Dec. 11,	23.938	Dec. 16,	23.833
Dec. 12,	23.818		
			(9 days)

Mean total pressure Dec. 8-Dec. 16 .....23.840 atms
Mean barom. pressure Dec. 8-Dec. 16 ..... 0.995 atms
Mean osmotic pressure Dec. 8-Dec. 16.....22.845 atms

TABLE XXVII.

0.9 Wt. normal solution. Expt. 3 at 30°. Cell R_3. Resistance 137,100 ohms. Manometer 24. Calc. gas pressure 22.244 atms. Time of setting up cell, Dec. 7, 1915. Barometer during final record: max., 1.004; min., 0.989. Total daily pressures:

Final Record.

Atms	Atms
Dec. 13, 23.814	Dec. 16, 23.813
Dec. 14, 23.820	Dec. 17, 23.770
Dec. 15, 23.835	

(5 days)

Mean total pressure Dec. 13-Dec. 17 .....23.810 atms
Mean barom. pressure Dec. 13-Dec. 17 ..... 0.996 atms
Mean osmotic pressure Dec. 13-Dec. 17 ....22.814 atms

TABLE XXVIII.

1.0 Wt. normal solution. Expt. 1 at 30°. Cell R_4. Resistance 183,300 ohms. Manometer 6. Calc. gas pressure 24.716 atms. Time of setting up cell, Dec. 10, 1915. Barometer during final record: max., 1.006; min., 0.975. Total daily pressures:

Final Record.

Atms	Atms
Dec. 15, 26.301	Dec. 18, 26.287
Dec. 16, 26.327	Dec. 19, 26.394
Dec. 17, 26.327	Dec. 20, 26.354

(6 days)

Mean total pressure, Dec. 15-Dec. 20.....26.333 atms
Mean barom. pressure Dec. 15-Dec. 20 ..... 0.997 atms
Mean osmotic pressure Dec. 15-Dec. 20 .....25.336 atms

TABLE XXIX.

1.0 Wt. normal solution. Expt. 2 at 30°. Cell R_{20}. Resistance 54,800 ohms. Manometer 39. Calc. gas pressure 24.716 atms. Time of setting up cell, Dec. 6, 1915. Barometer during final record: max., 1.004; min., 0.983. Total daily pressures:

Final Record.

Atms	Atms
Dec. 8, 26.289	Dec. 12, 26.186
Dec. 9, 26.185	Dec. 13,26.261
Dec. 10, 26.169	Dec. 14, 26.249
Dec. 11, 26.272	

(7 days)

Mean total pressure Dec. 8-Dec. 14 .....26.226 atms
Mean barom. pressure Dec. 8-Dec. 14 ..... 0.993 atms
Mean osmotic pressure Dec. 8-Dec. 14 .....25.233 atms

TABLE XXX.

1.0 Wt. normal solution. Expt. 3 at 30°. Cell R_{12}. Resistance 78,500 ohms. Manometer 53. Calc. gas pressure 24.716 atms. Time of setting up cell, Nov. 24, 1915. Barometer during final record: max., 1.008; min., 0.989. Total daily pressures:

Final Record.

Atms	Atms
Nov. 26, 25.288	Nov. 29, 26.145
Nov. 27, 26.211	Nov. 30, 26.167
Nov. 28, 26.081	Dec. 1, 26.197

(6 days)

Mean total pressure Nov. 26-Dec. 1 .....26.181 atms
Mean barm. pressure Nov. 26-Dec. 1 ..... 0.998 atms
Mean osmotic pressure Nov. 26-Dec. 1 .....25.183 atms

TABLE XXXI.

1.0 Wt. normal solution. Expt. 4 at 30°. Cell R_1. Resistance 100,000 ohms. Manometer 53. Calc. gas pressure 24.716 atms. Time of setting up cell, Dec. 10, 1915. Barometer during final record: max., 1.006; min., 0.975. Total daily pressures:

Final Record.

	Atms		Atms
Dec. 13,	26.040	Dec. 17,	26.090
Dec. 14,	26.065	Dec. 18,	26.098
Dec. 15,	26.050	Dec. 19,	26.171
Dec. 16,	26.073	Dec. 20,	26.150
			(8 days)

Mean total pressure Dec. 13-Dec. 20 .....26.092 atms
Mean barom. pressure Dec. 13-Dec. 20 ..... 0.995 atms
Mean osmotic pressure Dec. 13-Dec. 20 .....25.097 atms

TABLE XXXII.

Sol. No.	Weight Normality	Osmotic Pressure	Calc gas Pressures	Ration of O. P. to C. G. P.	Av. Ratio for each conc.	Deviation from av. ratio for all conc. (1.019)
(1)	0.1	2.529	2.472	1.022		
(2)	0.1	2.499	2.472	1.011	1.016	— .003
(3)	0.2	5.065	4.943	1,024		
(4)	0.2	5.027	4.943	1.017		
(5)	0.2	5.014	4.943	1.014	1.018	— .001
(6)	0.3	7.569	7.415	1.020		
(7)	0.3	7.552	7.415	1.018	1.019	± .000
(8)	0.4	10.016	9.886	1.013		
(9)	0.4	10.011	9.886	1.012	1.012	.007
(10)	0.5	12.685	12.358	1.026		
(11)	0.5	12.640	12.358	1.022		
(12)	0.5	12.621	12.358	1.021		
(13)	0.5	12.512	12.358	1.012	1.020	+ .001
(14)	0.6	15.098	14.830	1.018		
(15)	0.6	15.067	14.830	1.015		
(16)	0.6	15.056	14.830	1.015	1.016	— .003
(17)	0.7	17.819	17.301	1.034		
(18)	0.7	17.679	17.301	1.021		
(19)	0.7	17.562	17.301	1.014	1.023	+.004
(20)	0.8	20.301	19.773	1.026		
(21)	0.8	20.176	19.773	1.020		
(22)	0.8	20.112	19.773	1.015		
(23)	0.8	20.042	19.773	1.014		
(24)	0.8	20.025	19.773	1.011	1.017	— .002
(25)	0.9	22.842	22.244	1.027		
(26)	0.9	22.845	22.244	1.027		
(27)	0.9	22.814	22.244	1.025	1.026	+.007
(28)	1.0	25.336	24.716	1.025		
(29)	1.0	25.233	24.716	1.021		
(30)	1.0	25.183	24.716	1.018		
(31)	1.0	25.097	24.716	1.016	1.020	+.001

Av. Ratio for all concentrations = 1.019.

V. DISCUSSION OF TABLES.

Tables I to XXXI, inclusive, give a rather detailed account of the pressures developed in the cells after equilibrium was reached; in other words, after the final record was begun.

Table XXXII gives a summary of the osmotic pressures developed by the various concentrations of levulose solutions in the cells, and a comparison of these pressures with the theoretical gas pressures, which are calculated from the equation $Pv = Kt$ in which v is the volume of the pure solvent at its maximum density.

It will be seen that the osmotic pressures are excessive, i. e., they give a ratio with the theoretical gas pressures which is greater than unity. This excessive pressure would suggest that the solutions may have become concentrated before the final record was begun.

There are at least two ways in which the solutions could have become concentrated to a slight degree:

(1) If a cell is "set up" at a temperature a little lower than the temperature of the bath in which the measurements are made, a well-known "thermometer effect" will be noted. The cell contents and the liquids in the manometer upon expanding at this higher temperature, may force some of the solvent through the membrane, thus concentrating the enclosed solution.

(2) It is believed that certain sugars are capable of uniting with part of the solvent to form hydrates, especially at the lower temperatures. Past experience in measuring the osmotic pressures of cane sugar over wide ranges of temperature, goes to prove the presence of hydrates at the lower temperatures. A concentration will necessarily follow a union of the solvent molecules with those of the solute.

The first explanation is untenable for special precautions were taken to exert the initial mechanical pressure quickly, and to keep the whole system at thirty degrees

in the process of setting up. The depositing bath served for the latter purpose. The second explanation seems to be more nearly correct. It is believed that the excessive pressures, in the case of levulose solutions at thirty degrees, are due to the existence of hydrates in solution.

In almost every instance the solution which was taken from the cell showed a loss in rotation. At first sight this would appear to be due to dilution in the cell, brought about by imperfections in the membrane. Such a dilution has always characterized a low pressure. However, the greatest loss in rotation occurred in solutions which gave the higher pressures. Four cases will serve to show this strange behavior.

Sol. No.	Ratio of O. P. to C. G. P.	Loss in rotation
(12)	1.022	—1.5 degrees
(17)	1.034	—0.7 degrees
(25)	1.027	—3.0 degrees
(29)	1.021	—3.1 degrees

The statement has been made on another page that a fungus, a strain of penicillium glancum, creates much mischief in osmotic pressure work, by attacking the membranes. The measurements of levulose solutions were made at a time when the cells were known to be slightly infected by this pest. The solutions, when taken from the cells were of a greenish blue color and solid matter of the same color was found in suspension. In this way the presence of the pest was detected for it is known by experiment[21] that a growth of penicillium will give this coloration to a sugar solution in which there is placed some membrane material.

Immediately, every effort was made to suppress and destroy the pest by the usual and best method[22] that of soaking the cells in a saturated solution of thymol. The pest was never quite eradicated. However, after the

21 Ibid., p. 95.

22 Statements regarding penicillium and the methods of combating it will be found in the Monograph, pp. 94-95.

cells were treated in this way, the solutions which were taken from them were clearer and more transparent.

Although no special harm seemed to come to the membranes at this time, it is believed that the energies of the penicillium were directed against the sugar solutions and that the solute molecules were broken down into smaller or part molecules.

This tentative conclusion, the result of a careful consideration of the observed phenomena, serves to explain the loss in rotation of a solution whose pressure has been excessive. Furthermore, it led to believe that we could not justly correct the observed osmotic pressures for the seeming "dilution" as shown by the loss in rotation. These measurements would, in all probability, have more authority, if the penicillium had not been present and if the solutions had shown no loss in rotation.

VI. CONCLUSIONS.

The ratios of the osmotic pressures of levulose solutions at thirty degrees, to the theoretical gas pressures are fairly constant for the ten concentrations between and including 0.1N and 1.0N.

The excessive pressures are due without a doubt to the existence of hydrates in the solution at this temperature. This view is supported by the fact that cane sugar solutions exhibit like phenomena at this temperature.

The conclusion is further supported by the work performed in this laboratory by Mr. C. C. Minter, upon the freezing point lowerings of levulose solutions of the above concentrations. He found the average of the molecular lowerings to be 1°.92. This abnormal value seems to prove[23] that such solutions contain hydrates at the freezing point. It is believed that these hydrates are not broken down at thirty degrees.

23 Elements of Physical Chemistry, H. C. Jones, p. 237.

VII. BIOGRAPHY.

John Milton Blocher, Jr., was born February 24, 1891, in Gettysburg, Pa. He received his early education in the public schools of that place, graduating from the High School in 1908, after having completed a commercial course of study. He received his preparation for college in the Gettysburg Academy during the school year 1908-1909. He graduated from Pennsylvania College, Gettysburg, receiving the degree of Bachelor of Science in 1913. In the fall of 1913 he entered the Johns Hopkins University, taking Chemistry as his major subject; and Physical Chemistry and Mineralogy as his first and second minors respectively. He assisted Dr. Gilpin in the undergraduate laboratories during the school year 1914-1915.